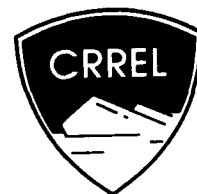


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**Microwave Digestion of
Soils and Sediments for
Assessing Contamination by
Hazardous Waste Metals**

Alan D. Hewitt and Charles M. Reynolds

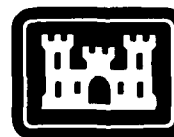
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Special Report 90-19



**U.S. Army Corps
of Engineers**
Cold Regions Research &
Engineering Laboratory

Microwave Digestion of Soils and Sediments for Assessing Contamination by Hazardous Waste Metals

Alan D. Hewitt and Charles M. Reynolds

June 1990



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PREFACE

This report was prepared by Alan D. Hewitt and Dr. Charles M. Reynolds, Research Physical Scientists, Geochemical Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory, under contract DA-2544-IAR-1689. Funding for this work was provided by the Program Manager, Rocky Mountain Arsenal, through the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), Durant Graves, Project Monitor.

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CONTENTS

Preface	ii
Introduction	1
Materials	1
Geological samples	1
Digestion apparatus	1
Digestion procedure	2
Heating cycles	2
Sample handling	3
Analysis	4
Results and discussion	4
RMA standard soil	5
Spike recoveries from RMA standard soil	5
NIST SRM-2704	6
Conclusions	7
Recommendations	7
Literature cited	8
Appendix A: Hot-plate digestion procedures	9
Appendix B: Instrument parameters	10
Appendix C: Analyte concentrations measured in the diluted digests	11
Abstract	15

ILLUSTRATIONS

Figure	
1. Modified microwave oven and digestion vessel	2

TABLES

Table	
1. Calibration of microwave oven by measurement of apparent power absorbed by 1 kg of water	2
2. Estimates of detection limit ($\mu\text{g/L}$) ($2\times$ variation in the baseline noise)	4
3. Metal concentrations ($\mu\text{g/g}$) reported for the RMA standard soil using USATHAMA method R9 and those determined with the microwave- HNO_3 digestion procedure	5
4. Spike recoveries from the RMA standard soil using the microwave HNO_3 digestion procedure	6
5. NIST certified values and determined metal concentrations ($\mu\text{g/g}$) for the microwave- HNO_3 digestion of the SRM-2704 river sediment	6
6. Comparison of analyte recoveries using HNO_3 and HNO_3 -HF acids for the microwave digestion	7

Microwave Digestion of Soils and Sediments for Assessing Contamination by Hazardous Waste Metals

ALAN D. HEWITT AND CHARLES M. REYNOLDS

INTRODUCTION

Microwave ovens have been used to digest biological samples for over two decades (Abu-Samra et al. 1975, Barret et al. 1978). Investigators have also used microwave-heated-acid digestions for the dissolution of metals from geological materials (Matthes et al. 1983, Nadkarni 1984, Smith et al. 1985, Fisher 1986, Lamothe et al. 1986, Mahan et al. 1987). Kammin and Brandt (1989a,b) compared microwave digestions and the established EPA protocol for the extraction of metals from a laboratory control sample and an environmental reference standard. A brief outline of both the EPA SW-846, method 3050, and USATHAMA R9 hot-plate digestion protocols can be found in Appendix A.

Most microwave dissolution procedures developed for soil and sediment samples employ closed vessels; thus, digestion occurs under both elevated temperature and pressure. The motivation for using microwave energy in the digestion of samples is to reduce the time required compared to hot-plate techniques. Commercial microwave digestion systems are now available from at least four companies—CEM, Prolabo, Floyd and GT—and a software program is currently being developed to provide guidelines for preparing samples (Settle et al. 1989). However, several researchers have used relatively inexpensive residential-grade microwave ovens successfully for closed vessel digestions (Matthes et al. 1983, Nadkarni 1984, Smith et al. 1985, Lamothe et al. 1986, Aysola et al. 1987, Manhan et al. 1987).

The objective of this study was to evaluate a microwave digestion technique relative to the certified USATHAMA R9 method for the extraction of metals in soils and sediments. Sample preparation time, overall simplicity, field compatibility and extraction efficiency were considered. Our method uses a slightly modified residential-grade microwave oven, 120-mL Teflon digestion vessels, 10 mL of concentrated HNO_3 per sample and a rotating carousel for the extraction of metals from 0.5-g samples. Guidelines are provided for

employing residential-grade microwave ovens for closed vessel extraction of hazardous waste metals from 12 soil or sediment samples in less than 13 minutes. Neither method R9, the EPA's SW-846, method 3050, nor the microwave- HNO_3 digestion method developed was designed to measure the total amount of metals in soils or sediments. Instead, these methods are geared for extracting those metals potentially available to natural leaching and biological processes.

MATERIALS

Geological samples

The two sample materials used were the National Institute of Standards and Technology (NIST) standard reference material 2704 (SRM-2704), Buffalo River sediment, and a Rocky Mountain Arsenal (RMA) standard soil.* Digests of both the NIST SRM-2074 and the RMA standard were analyzed for native concentration of metals, and a spike recovery test was also done on the RMA soil.

Digestion apparatus

A Sanyo Model EM-663A, 750-W, residential-grade microwave oven was modified for our digestion experiments. This oven has a 0.04-m³ cavity, rear exhaust vents and a plastic-enamel interior. To facilitate air exchange inside the oven cavity, the rear exhaust vents were covered by a Lucite manifold that housed a 105-mm-diameter, 1.8-m³/min cooling fan (Archer). The fan pulled air through the oven vents and channeled the exhaust from the manifold into a laboratory exhaust hood. A commercially available wind-up carousel rotated the digestion vessels so that all samples received equal dosages of the microwave energy.

*Available through the Program Managers Office, Rocky Mountain Arsenal, Commerce City, Colorado 80022.

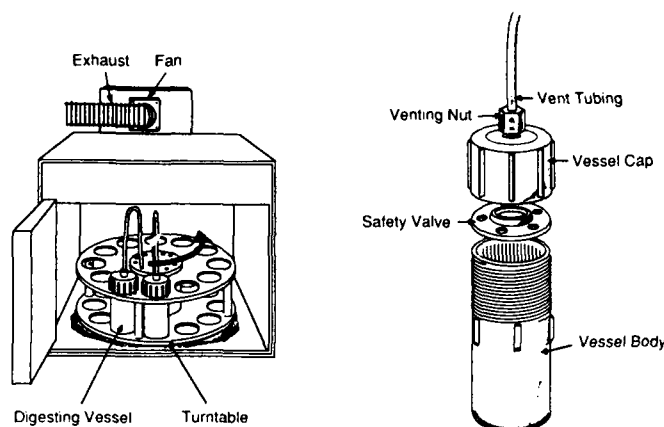


Figure 1. Modified microwave oven and digestion vessel.

Samples were digested in 120-mL Teflon (PFA-poly(tetrafluoroethylene)) vessels. A set of 12 digestion vessels, with holding tray, relief valves, vent tubing and capping station, was obtained from the CEM Corp., Indian Trail, North Carolina. The capping station sealed the digestion vessels with a constant 16.3-Nm torque and also allowed us to open the vessels in a controlled manner. The sealed vessels were designed to withstand an internal pressure of 8.2 atm (831 kPa). A schematic of both the modified microwave oven and digestion vessel is shown in Figure 1.

DIGESTION PROCEDURE

Heating cycles

Both the energy delivered to the oven cavity and the energy absorbed by the oven contents are critical factors in the development of a digestion program. Failure to establish these two parameters can lead to vessel ruptures and oven malfunctions, which are potentially hazardous to the operators (Gilman and Grooms 1988). Additionally, the presence of large amounts of triglycerides, fats or fatty acids in samples may produce nitroglycerine during microwave digestion in a closed vessel (Kammin and Brandt 1989b).

Kingston and Jassie (1986, 1988) provide guidelines for determining the power delivered by microwave ovens and for predicting the power absorbed by different digestion solutions. The apparent power absorbed by the extraction solution is given by

$$P = C_p K \Delta T m / t \quad (1)$$

where P = apparent power absorbed (W)

C_p = heat capacity (cal/g °C)

K = constant for converting calories to watts

ΔT = change in temperature (°C)

m = mass (g)

t = time (s).

This equation is best suited for describing the energy transmitted by a microwave oven during a 2- to 4-minute heating period for a liquid mass that is greater than 500 g, initially at room temperature, and contained in a microwave-transparent, open vessel. Kingston and Jassie (1988) recommend that microwave oven power be determined by heating 1 kg of water in a thick-walled Teflon or polyethylene vessel for at least 2 minutes at full power, stirring and measuring the temperature. Table 1 shows the results obtained when we calibrated

Table 1. Calibration of microwave oven by measurement of apparent power absorbed by 1 kg of water.

t (s)	T_i (°C)	T_f (°C)	ΔT	P (W)*
90	20	33	13	604
120	20	37	17	593
150	20	42	22	614
180	21	47	26	604
210	21	51	30	598
240	21	56	35	610

\bar{X} = 604.

Standard deviation = 7.7.

* Calculated using eq 1.

the Sanyo microwave oven. Since an oven's magnetron degrades with use, the apparent power should be re-measured periodically.

Owing to heat loss and changes in heat capacity of a solution, eq 1 fails to describe the power absorbed at high temperatures and after heating for periods longer than several minutes (Kingston and Jassie 1988). Consequently, our ability to predict solution temperatures using eq 1 is very limited. However, experimental heat absorption curves for different digestion solutions as a function of mass have been published (Kingston and Jassie 1988).

The microwave digestion procedure developed for this study was similar to the method published by CEM Corporation for the extraction of metals from soils (CEM Corp. 1988). We altered the CEM method by decreasing the microwave heating periods and leaving out the hydrogen peroxide to further oxidize organic matter after the heated-acid digestion. The heating cycles were decreased to compensate for the greater level of power delivered by the Sanyo microwave oven compared to the CEM oven. To maintain the same temperatures and pressures in our system as in the CEM system, heating times were multiplied by the ratio of the power of the CEM oven and the Sanyo oven (570/604):

CEM	Step 1—2:30 minutes at high. Step 2—10:00 minutes at 80%.
CRREL	Step 1—2:20 minutes at high. Step 2—9:25 minutes at 80%.

Pressure is also a function of the organic composition of the soil or sediment being digested. Ultimate pressures and temperatures will vary from sample to sample. The carbon percentage was 3.35 for the SRM-2704, but it was not reported for the RMA standard soil. To streamline the method for field deployment, this initial study used only nitric acid. Similarities between the procedures were sample size (0.5 g), use of twelve 120-mL vessels, 10 mL of 16-M HNO_3 per vessel and the oven geometry.

Sample handling

To prepare the samples, approximately 0.5-g portions of samples were weighed to the nearest milligram and transferred to the Teflon microwave digestion vessels, 10 mL of redistilled G. Fredrick Smith (GFS) nitric acid was added and the lid tightened with the CEM capping station. The sealed vessels were placed in the microwave tray and the vent tubes attached. Once all 12 positions were filled, the tray was positioned in the middle of the microwave oven on top of a rotating

carousel. With the oven door closed and the manifold fan on, we began the two-step heating program.

After microwave treatment, the entire tray of vessels was placed in a cold water bath for 15 minutes to cool and reduce internal pressure. Once cooled, we opened the individual vessels at the capping station inside a laboratory exhaust hood to protect personnel from the nitric acid fumes. Microwave digestions of the river sediment and RMA soil with HNO_3 generated reddish-brown and light brown gases, respectively, inside the vessels. In both cases a particulate residue remained after digestion. Digests were diluted by adding 90 mL of deionized water (Milli-Q, Millipore Corp.) to each vessel. We have determined that there was very little volume reduction (less than 0.2 mL) for the HNO_3 acid during the closed vessel digestions. After swirling the diluted digests, we took 5-mL aliquots for analysis and filtered them through a 0.45- μm Millex-HV Durapore membrane filter (Millipore Corp.) using a 10-mL Luer Lok syringe (Becton Dickinson). The syringe was only half filled to prevent direct contact between the 10% v/v HNO_3 solution and rubber-tipped plunger. The filter and syringe were conditioned by passing and discarding an initial 5-mL aliquot. Filtration was not necessary for the Hg determinations because this analyte is removed from the aqueous solution as a gas prior to detection. Diluted digests were stored in acid-washed, 7.5-mL low density polyethylene bottles (Nagle). We prepared procedural blanks by taking 10 mL of HNO_3 through the digestion, dilution and filtering steps.

To prevent volatilization of Hg, Se and As, the soil and sediment samples were not oven-dried prior to digestion. We based analyte concentrations on dry weight after correcting for moisture content determined from paired samples. The SRM-2704 was used as received. We mechanically dispersed the RMA soil by grinding it with the bottom of a quartz beaker in an aluminum weighing dish. Large RMA soil particles (more than 1 mm in diameter) were discarded.

We prepared spike recovery samples by adding 50- μL aliquots of aqueous standards to weighed portions of RMA standard soil in the digestion vessel. Sequential 50- μL additions were made until a 2:1 (w/w) soil-to-aqueous mixture was reached ($5 \times 50 \mu\text{L}$ per 0.5 g soil). We equilibrated this slurry for approximately 1 hour prior to adding 10 mL of HNO_3 and digesting as recommended by USATHAMA procedure R9. All of the analyte spike additions were made from individual 400-mg/L solutions (spike = 20 μg), except Ba, which was made from a 1000-mg/L solution (spike = 50 μg).

To limit cross contamination between samples, the vessels were rinsed with deionized water, carried through the digestion heating cycles with only HNO_3 and then rinsed again with deionized water. This procedure is

Table 2. Estimates of detection limit ($\mu\text{g/L}$) ($2\times$ variation in the baseline noise).

Analyte	Detection limit
Ag	≤ 0.5
As	≤ 0.4
Ba	≤ 2.0
Cd	≤ 0.2
Cr	≤ 0.4
Cu	≤ 0.5
Hg	≤ 0.005
Ni	≤ 0.3
Pb	≤ 0.5
Se	≤ 1.0
Tl	≤ 0.5
Zn	≤ 0.3

particularly important in the analysis of samples potentially contaminated with hazardous wastes because a wide range of metal concentrations is frequently encountered. Blanks digested in vessels that previously had been used to digest the NIST SRM-2704, the RMA standard soil or the spiked RMA standard soil and only rinsed with deionized water showed no detectable cross contamination. No analyte concentrations for the procedural blanks or cross-contamination checks were above levels corresponding to two times the variation in the baseline noise (Table 2). Since analyte concentrations measured in the soil and sediments extracts were typically an order of magnitude above this level of uncertainty (Hg in the RMA soil being the only level less than an order of magnitude above two times the base line variation), this level was taken as estimate of the detection limit. Concentrations of metals determined in sample extracts were not blank corrected.

ANALYSIS

The metals investigated were silver (Ag), arsenic (As), barium (Ba), cadmium (Cd), copper (Cu), chromium (Cr), mercury (Hg), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), thallium (Tl) and zinc (Zn). Only spike recoveries were reported for Ag and Se since certified or previously established values did not exist, and there were no successful recoveries of Sb from the digested soil and sediment with the microwave- HNO_3 digestion. However, a microwave heated digestion using both HNO_3 and HCl acids recovered Sb from the NIST SRM-2704 sediment (Appendix C). Metal concentrations in extracts were determined by Graphite Furnace Atomic Absorption (GFAA), except for Hg, which was done by Cold Vapor Atomic Absorption (CVAA). Settings for a Perkin-Elmer (PE) model 403 Atomic

Absorption Spectrophotometer (AAS) and a PE model 2200 heated graphite atomizer can be found in Appendix B. Analyte concentrations measured in solution digests are reported in Appendix C.

We determined mercury by CVAA, following a modified Hatch and Ott (1968) procedure. Sample digests ranging from 1 to 48 mL were used for the Hg determinations. The digests were chemically reduced with 2 mL of 10% v/v stannous chloride and then sparged with Hg-free air. The reduced Hg passed through a magnesium perchlorate water-vapor trap into an optical cell designed to enhance detection (Tuncel and Atoman 1980). Mercury was determined within 2 hours of sample digestion to limit vapor contamination associated with the gas permeability of plastic containers (Cragin 1979).

With the exception of Hg, all analyte concentrations in the digests were determined by the method of single standard addition (Perkin-Elmer 1981). Mercury concentrations were established by direct comparison to the aqueous standards. Analyte concentrations in the digests were based on the average of at least two instrument responses on a strip chart recorder.

The instrument was calibrated for each analyte to establish the range of linearity and the presence of an intercept. Aqueous calibration standards were prepared by diluting 1000 mg/L of certified atomic absorption stock solutions (Fisher Scientific Co., J.T. Baker Co., AESAR/Johnson Matthey Inc.). Working standards were prepared in deionized water (Milli-Q, Millipore Corp.) that was acidified to 2% (v/v) with GFS nitric acid. For each metal, the instrument calibration was based on at least three different concentration standards that were each analyzed in triplicate. We calculated slopes and intercepts by least-squares regression and tested the intercepts using analysis of variance for significant difference from zero at the 95% confidence level by comparing residuals to residuals calculated from a zero intercept regression equation. We determined that significant intercepts were caused by the instrument furnace blank, and thus analyte responses were corrected accordingly. It was necessary that the intercepts be distinguished as being caused either by blanks or an instrument response for the determination of metal concentrations; thus, calibration curves, blanks and instrument noise required investigation.

RESULTS AND DISCUSSION

The microwave- HNO_3 digestion, digest dilution and filtering procedure used for the extraction of metals from soil and sediments took less than 30 minutes from start to finish. An individual employing several 12-

Table 3. Metal concentrations ($\mu\text{g/g}$) reported for the RMA standard soil using USATHAMA method R9 and those determined with the microwave- HNO_3 digestion procedure.

	<i>Ba</i>	<i>Cu</i>	<i>Cr</i>	<i>Hg</i>	<i>Ni</i>	<i>Pb</i>	<i>Zn</i>
USATHAMA R9	139.8	9	8.8	0.008	10.1	13	43.1
Microwave- HNO_3	149	10.3	10.2	0.0066	13.8	8.7	37.7
	143	10.6	11.6	0.0072	6.6	9.5	50.0
	131	10.6	12.3	0.0073	13.5	9.3	44.5
	133	10.3	10.7		12.4	9.0	43.6
	143	10.1	10.8		11.7	9.6	37.2
\bar{X} =	140	10.4	11.1	0.0070	11.6	9.2	42.6
Std. dev.	7.6	0.22	0.83	0.0004	2.9	0.37	5.3

position sample carousels with vessels could digest and prepare for analysis approximately 100 samples daily. The method requires only a balance, microwave oven, digestion vessels, capping station, concentrated HNO_3 acid, reagent grade water, and disposable syringes and filters.

The limited requirements for materials and support apparatus, such as electricity and an exhaust hood, make this sample preparation method compatible with field-mobile laboratories. For field application one advantage of the microwave- HNO_3 digestion protocol over existing hot-plate techniques is that hood space is required for only the capping station and exhaust hose. The number of simultaneous digestions that could be run with hot-plate methods in a portable laboratory would be limited by available hood space. Additionally, this microwave procedure uses only HNO_3 , thereby simplifying field preparation. Other advantages of the microwave- HNO_3 digestion are that it requires very little wet chemistry, is less subjective and does not expose the sample to dry heat. Hot-plate digestion methods may require repetitive additions and heating cycles until organic decomposition is judged complete. Because hot-plate digestions use open vessels, each evaporation cycle can leave portions of the substrate dry, even though it does not dry completely. Soil or sediment digests that are partially or totally dried may lose volatile analytes. Volatilization losses of organo-mercury compounds in soils dried at 60°C (Iskandar et al. 1972) or digested in open systems (Van Delft and Vos 1988) has been documented.

RMA standard soil

The concentration of metals determined in the microwave- HNO_3 digests and those reported by another laboratory using the USATHAMA R9 digestion procedure for the RMA standard soil are presented in

Table 3. Our values represent determinations obtained from three to five replicates of the RMA soil that were digested and analyzed simultaneously. For Ba, Cr, Cu, Hg, Ni, Pb and Zn, the concentrations determined using the microwave digestion procedure ranged from 127 to 71%, with an overall average of 102% of those obtained by the hot-plate procedure.

Both the R9 and microwave- HNO_3 digestion methods are designed for determining metals in soil and sediments contaminated by hazardous waste. The native levels of metals in the RMA standard soil were low compared to crustal averages (Taylor 1964), thus not indicative of contamination. Prior to analysis of the RMA soil, a portion of the bulk sample supplied by RMA must be ground and sieved by the analyst. The heterogeneity within the bulk soil samples most likely influences variability in the metal content. The low levels of native metals in the soil and inherent variability of the bulk material provided for analysis must be considered when comparing the results obtained by both procedures. Regardless, this interlaboratory-intermethod comparison shows that both digestion procedures extract similar quantities of metals from the RMA soil.

Spike recoveries from RMA standard soil

Average recoveries of the analytes spiked onto the RMA standard soil ranged from 90 to 103%, except that there was no discernible recovery of Sb. The overall average recovery for the 12 metals was 97% (Table 4). The metals were determined on a set of three samples that were spiked, digested and analyzed simultaneously. These results indicated that the microwave digestion was not susceptible to losses or contamination for the analytes determined. Quantitative recoveries of Hg and Se demonstrated that microwave digestion in closed vessels was an acceptable method for volatile metals.

Table 4. Spike recoveries from the RMA standard soil using the microwave-HNO₃ digestion procedure.

<i>Metal</i>	<i>Ag</i>	<i>As</i>	<i>Ba</i>	<i>Cd</i>	<i>Cr</i>	<i>Cu</i>	<i>Hg</i>	<i>Ni</i>	<i>Pb</i>	<i>Se</i>	<i>Tl</i>	<i>Zn</i>
Spike (µg)	20	20	50	20	20	20	20	20	20	20	20	20
Average % recovery	99	98	103	102	92	95	97	100	95	98	97	90
Std. dev.	1.2	14	8.4	3.2	3.8	1.1	2.9	11	0.6	2.8	2.3	16

Van Delft and Vos (1988) have also shown that organic forms of Hg can be quantitatively recovered with a microwave-heated-acid digestion in a closed vessel.

There was no Sb detected by GFAA in the microwave-HNO₃ digests from RMA soils spiked with Sb or from the NIST SRM-2704 reference material. We obtained quantitative recoveries when Sb was spiked into 10 mL of HNO₃ and then digested. Additionally, aliquots of a Sb standard solution added to a RMA soil digest in proportions ranging from 0 to 50% prior to analysis were quantitatively recovered. However, losses exceeded 70% when Sb was spiked into the RMA digests (10 mL of HNO₃ and 0.5 g of soil) between two consecutive microwave heating programs. These findings can be explained by the hydrolysis of Sb by oxidizing acids.* Formation of insoluble Sb-oxides can be prevented by using HCl in the extraction solution. When a 50/50 mixture of HNO₃ and HCl was used as the digestion acid with the microwave heating, greater than 75% of the Sb in NIST SRM-2704 was recovered (Appendix C).

*Personal communication with Steve Matthes, U.S. Department of the Interior, Bureau of Mines, Albany, Oregon.

Overall spike recoveries were reasonably quantitative. Those metals observed to have the poorest recoveries (Zn and Cr—92% or less) and/or the largest coefficients of variation (As, Ba, Ni and Zn—greater than 8%) had spike-to-background ratios less than 3.0. Provost and Elder (1983) have statistically shown that, as this ratio decreases, percent recovery of spiked analytes become less quantitative.

NIST SRM-2704

Table 5 shows the results for the concentrations of metals determined by the microwave-HNO₃ digestion of the NIST SRM-2704 river sediment. Mean recoveries of the NIST certified values for As, Cd, Cu, Pb, Tl and Zn averaged 102%. The average Ni recovery was about 10% less than the NIST certified value, and Ba, Cr and Hg were even lower. NIST certification of metal concentrations in the SRM-2704 sediment was based on at least two independent methods, usually neutron activation analysis and a wet digestion method using hydrofluoric acid (HF) in conjunction with other acids prior to analysis by AAS or Inductively Coupled Plasma (ICP) atomic emission spectroscopy. Clearly, both techniques are designed to measure total metal concen-

Table 5. NIST certified values and determined metal concentrations (µg/g) for the microwave-HNO₃ digestion of the SRM-2704 river sediment.

	<i>As</i>	<i>Ba</i>	<i>Cd</i>	<i>Cr</i>	<i>Cu</i>	<i>Hg</i>	<i>Ni</i>	<i>Pb</i>	<i>Tl</i>	<i>Zn</i>
NIST	23.4 ± 0.8*	414 12	3.45 0.22	135 5	98.6 5.0	1.44 0.07	44.1 3.0	161 17	1.2 0.2	438 12
Microwave-HNO ₃	23.7 23.1 23.6	81 89 108	3.63 3.65 3.60	87.8 82.7 83.0	98.7 95.4 94.7	1.10 1.09 0.96	38.1 39.2 39.3	164 168 172	1.37 1.18 1.27	463 425 451
\bar{X} =	23.5 ± 0.8*	92.6 34.5	3.63 0.06	84.5 7.1	96.3 5.2	1.05 0.19	38.9 1.7	168 9.9	1.27 0.24	446 48
% Recovery										
\bar{X} =	100	22.4	105	62.6	97.6	72.9	87.4	104	106	102
Std. dev.	1.4	3.3	1.1	2.1	2.2	5.4	2.8	2.5	7.9	4.5

* 95% uncertainty limits.

Table 6. Comparison of analyte recoveries using HNO₃ and HNO₃-HF acids for the microwave digestion.

	<i>River sediment SRM-2704</i>			<i>RMA standard soil</i>		
	<i>NIST</i> ($\mu\text{g/g}$)	<i>Average % recovery</i> <i>and std. dev.</i>		<i>USATHAMA</i> <i>R9</i> ($\mu\text{g/g}$)	<i>Average % recovery</i> <i>and std. dev.</i>	
		<i>HNO₃</i>	<i>HNO₃-HF</i>		<i>HNO₃</i>	<i>HNO₃-HF</i>
Ba	414	22.4 \pm 3.3	73.8 \pm 1.2	139.8	100 \pm 5.4	356 \pm 171
Cd	3.45	105 \pm 1.1	99.6 \pm 1.3	< 0.3	NA	NA
Cu	98.6	97.6 \pm 2.2	95.9 \pm 4.8	9	116 \pm 2.4	129 \pm 1.0
Cr	135	62.6 \pm 2.1	76.4 \pm 3.0	8.8	126 \pm 9.0	251 \pm 21.4
Ni	44.1	87.4 \pm 2.8	112 \pm 4.9	10.1	115 \pm 27.7	185 \pm 10.1
Pb	161	104 \pm 2.5	94.8 \pm 2.5	13	70.7 \pm 2.8	172 \pm 5.1
Zn	438	102 \pm 4.5	97.6 \pm 3.9	43.1	98.8 \pm 11.8	95.4 \pm 7.5

tration. In contrast, the microwave-HNO₃ extraction does not dissolve metals contained in the lattice of many aluminosilicates. Kammin and Brandt (1989a,b) compared microwave digestion to the EPA SW-846, method 3050, and reported that both the microwave and hot-plate methods recovered similar amounts of metals from an EPA laboratory control sample, yet neither method quantitatively recovered all metals from the NIST SRM-1646 estuarine sediment compared to the NIST certified values.

We also digested the NIST SRM-2704 using HNO₃-HF (8:2, v/v) with the same microwave program used for the HNO₃ digestion. Following digestion, we diluted the acid mixture digest to 100 mL with 1.1% boric acid to dissolve any insoluble metal fluorides that may have formed (Bernas 1968). Average recoveries obtained for the HNO₃-HF mixture appear in Table 6. Clearly, the recoveries for both Ba and Cr improved for the HNO₃-HF digestion of the NIST SRM-2704. The RMA standard soil was also digested with HNO₃-HF (Table 6). Several metal concentrations determined after the HNO₃-HF microwave digestion increased greatly, demonstrating that both the present USATHAMA protocol and the proposed microwave-HNO₃ digestion procedure do not recover total quantities of some metals from this soil.

It is well documented that digestion methods employing HNO₃ or HNO₃-HCl mixtures and heated with either a hot-plate or microwave oven do not extract total quantities of many native metals from geological samples. In general, wet digestions, excluding HF, extract those components potentially available through natural biological and leaching processes, and do not attack the aluminosilicate matrix (Que Hee and Boyle 1988). Fortunately, this fraction or portion usually represents the hazardous waste contribution, since the preponderance of anthropogenic metals in soil and sediments are associated with the organic fraction and clay surfaces.

CONCLUSIONS

1. Residential grade microwave ovens can be equipped for closed vessel extractions of metals from geological materials.
2. In the RMA standard soil, concentrations of Ba, Cd, Cu, Hg, Ni, Pb and Zn estimated by the microwave-HNO₃ digestion were within 30% of those reported using the USATHAMA procedure R9.
3. The microwave-HNO₃ digestion recovered better than 90% of the following analytes spiked onto the RMA standard soil: Ag, As, Ba, Cd, Cr, Cu, Hg, Pb, Ni, Se, Tl and Zn.
4. The microwave-HNO₃ digestion extracted better than 94% of the NIST certified levels of As, Cd, Cu, Pb, Tl and Zn from the SRM-2704 reference river sediment.
5. Metals can be extracted from geological materials contaminated by hazardous waste in less than 13 minutes employing a closed vessel microwave digestion method versus several hours for existing hot-plate methods.
6. Closed vessel microwave extractions are more routine and are less prone to volatile metal losses than open vessel digestions.

RECOMMENDATIONS

Compared to the USATHAMA procedure R9 for dissolution of metals from contaminated soil and sediments, closed vessel microwave digestions are quicker, require less wet chemistry and less support equipment, and are not subject to losses of volatile metals. For these reasons, microwave procedures are adaptable to the field and should be considered for program validation. A sound program would require well-prepared geological materials for intercalibration among laboratories. Appropriate sample materials should be available in

sets consisting of both uncontaminated and contaminated samples. Soils and sediments having a range of properties would be needed to effectively evaluate any digestion procedure.

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APPENDIX A: HOT-PLATE DIGESTION PROCEDURES

The following are general outlines of the hot-plate digestion procedures certified by the EPA and USATHAMA for the preparation of samples for the analysis of hazardous waste metals.

Summary of the SW-846, method 3050, digestion

This method is used to prepare sediment, sludges and soil samples for analysis by flame, furnace atomic absorption and inductively coupled plasma.

1. Mix sample thoroughly, then weigh a 1.00- to 2.00-g portion to the nearest 0.01 g and transfer to a conical beaker.

2. Add 10 mL of 1:1 HNO_3 , mix the slurry and cover the beaker with a watch glass. Heat the sample on a hot plate to 95°C and reflux for 10 to 15 minutes without boiling. Cool, then add 5 mL of concentrated HNO_3 , cover and reflux for an additional 30 minutes. Repeat this last step to ensure complete oxidation. While it is still covered with a ribbed watch glass, allow the solution to evaporate to 5 mL without boiling or losing solution coverage on the bottom of the beaker.

3. After sample has cooled, add 2 mL of Type II water and 3 mL of 30% H_2O_2 . Cover the beaker with the watch glass and return to hot plate for warming. Care must be taken to ensure that losses do not occur because vigorous effervescence. Heat until effervescence subsides, then cool the sample.

4. Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. NOTE: Do not add more than 10 mL of 30% H_2O_2 .

Summary of method R9

This method is used for the analysis of Cd, Cr, Cu, Pb and Zn in soils and sediments.

1. Weigh a 1.0-g portion of a sample quantitatively and transfer to 100-mL beaker.

2. Add 3.0 mL of concentrated HNO_3 , cover the beaker with a watch glass, place it on the hot plate, evaporate to near dryness, then cool it.

3. Repeat Step 2 until digestion is complete.

4. Add 2.0 mL of 1:1 HNO_3 and 2.0 mL of 1:1 HCl to the residue and heat until it dissolves.

APPENDIX B: INSTRUMENT PARAMETERS

<i>Metal</i>	<i>Ag</i>	<i>As</i>	<i>Ba</i>	<i>Cd</i>	<i>Cu</i>	<i>Cr</i>	<i>Hg</i>	<i>Ni</i>	<i>Pb</i>	<i>Sb</i>	<i>Se</i>	<i>Tl</i>	<i>Zn</i>
Drying temp (°C)	120	120	120	120	120	120	—	120	120	120	110	120	120
Drying time (s)	20	30	24	16	20	25	—	25	20	40	26	24	15
Ashing temp (°C)	500	850	1500	250	900	1200	—	1000	450	1000	1150	400	400
Ashing time (s)	10	15r*	10	10	10	10	—	10	10	10	10r/10h*	10	10
Atomization temp (°C)	2500	2750	2600	2300	2700	2750	—	2750	2300	2750	2700	2350	2200
Atomization time (s)	5	4	10	4	5	6	—	5	5	4.5	5	5	4
Wavelength (nm)	328	193	554	229	325	358	257	232	283	218	196	277	214
Slit width (nm)	0.7	0.7	0.2	0.7	0.7	0.7	0.7	0.2	0.7	0.2	0.2	0.2	0.7
Volume of sample (μL)	10	20	20	10	20	20	—	20	20	50	50	20	10
Sheathing gas	Ar	Ar	Ar	Ar	Ar	Ar	Air	Ar	Ar	Ar	Ar	Ar	Ar
Gas flow (cm ³ /min)	55	15	40	105	15	55	470	15	30	15	15	30	160
Gas interrupt	N7	S3	N7	N7	N7	N7	—	N7	N7	N7	N7	S7	N7
Graphite tube	Carb.†	Pyro.	Pyro.	Carb.	Carb.	Carb.	—	Pyro.	Carb.	Carb.	Pyro.	Carb.	Carb.
Matrix modifier	—	**	—	—	—	—	—	—	—	—	**	—	—

*r = ramp, h = hold

†Carb. = carburized; pyro. = pyrocoated.

** 0.015 mg Pb + 0.01 mg Mg(NO₃)₂

APPENDIX C: ANALYTE CONCENTRATIONS MEASURED IN THE DILUTED DIGESTS

All RMA standard soil values and NIST SRM-2704 reference sediment values have been corrected for moisture (3.0% and 0.8% respectively).

Table C1. Metal concentrations ($\mu\text{g/L}$) measured in the microwave- HNO_3 digest of the RMA standard soil (Table 3).

<i>Soil weight (g)</i>	<i>Ba</i>	<i>Cu</i>	<i>Cr</i>	<i>Ni</i>	<i>Pb</i>	<i>Zn</i>	<i>Hg</i>
0.544	37.5	27.3	26.8	18.2	15.3	9.5	—
	*(2100)	(200)	(200)	(400)	(300)	(2100)	—
0.529	35.0	27.3	29.8	11.3	16.3	12.2	—
	(2100)	(200)	(200)	(300)	(300)	(2100)	—
0.524	31.6	27.0	31.3	17.2	15.7	10.8	—
	(2100)	(200)	(200)	(400)	(300)	(2100)	—
0.545	33.4	27.3	28.3	16.4	15.8	11.0	—
	(2100)	(200)	(200)	(400)	(300)	(2100)	—
0.541	35.8	26.4	28.4	15.4	16.8	9.3	—
	(2100)	(200)	(200)	(400)	(300)	(2100)	—
0.655	—	—	—	—	—	—	0.040
	—	—	—	—	—	—	(104)
0.715	—	—	—	—	—	—	0.048
	—	—	—	—	—	—	(104)
0.705	—	—	—	—	—	—	0.048
	—	—	—	—	—	—	(104)

*Dilution factor (mL).

Table C2. Metal concentrations ($\mu\text{g/L}$) measured in the microwave- HNO_3 digest of the NIST SRM-2704 reference sediment (Table 5).

<i>Sediment weight (g)</i>	<i>As</i>	<i>Ba</i>	<i>Cd</i>	<i>Cr</i>	<i>Cu</i>	<i>Ni</i>	<i>Pb</i>	<i>Tl</i>	<i>Zn</i>	<i>Hg</i>
0.528	20.7	38.4	9.50	28.7	32.3	18.1	53.8	3.33	10.5	—
	*(600)	(1100)	(200)	(1600)	(1600)	(1100)	(1600)	(200)	(23,100)	—
0.500	19.1	40.0	9.04	25.6	29.6	17.7	52.0	2.93	9.1	—
	(600)	(1100)	(200)	(1600)	(1600)	(1100)	(1600)	(200)	(23,100)	—
0.526	20.5	51.2	9.39	27.0	30.9	18.6	56.2	3.57	10.2	—
	(600)	(1100)	(200)	(1600)	(1600)	(1100)	(1600)	(200)	(23,100)	—
0.736	—	—	—	—	—	—	—	—	—	0.16
	—	—	—	—	—	—	—	—	—	(5000)
0.832	—	—	—	—	—	—	—	—	—	0.18
	—	—	—	—	—	—	—	—	—	(5000)
0.526	—	—	—	—	—	—	—	—	—	0.10
	—	—	—	—	—	—	—	—	—	(5000)

*Dilution factor (mL).

Table C3. Metal concentrations ($\mu\text{g/L}$) measured in the microwave- HNO_3 digest of the spiked RMA standard soils (Table 4). Spike recoveries calculated with the background concentrations removed.

<i>Ag</i>	<i>As</i>	<i>Ba</i>	<i>Cd</i>	<i>Cr</i>	<i>Cu</i>	<i>Hg</i>	<i>Ni</i>	<i>Pb</i>	<i>Se</i>	<i>Tl</i>	<i>Zn</i>
17.7	19.7	47.9	9.94	16.1	24.0	0.18	13.2	12.1	17.2	17.8	11.9
*[18.2]	[20.8]	[48.8]	[9.52]	[17.6]	[24.8]	[0.19]	[13.4]	[12.6]	[18.2]	[18.8]	[12.6]
†{0.0}	{8.3}	{32.9}	{0.0}	{5.1}	{6.7}	{0.00}	{3.9}	{3.1}	{0.0}	{0.0}	{7.7}
18.1	23.5	35.7	9.94	23.4	24.5	0.19	12.9	12.5	18.1	12.8	12.3
[18.2]	[21.8]	[34.4]	[9.52]	[25.0]	[25.6]	[0.19]	[13.9]	[13.0]	[18.2]	[12.9]	[11.9]
{0.0}	{9.3}	{22.5}	{0.0}	{6.8}	{7.4}	{0.00}	{4.3}	{3.4}	{0.0}	{0.0}	{7.0}
18.1	20.7	39.1	9.38	25.5	25.2	0.18	15.0	12.7	18.0	12.6	12.1
[18.2]	[22.1]	[38.6]	[9.52]	[26.3]	[25.9]	[0.19]	[14.0]	[13.1]	[18.2]	[12.9]	[13.2]
{0.0}	{9.6}	{26.7}	{0.0}	{8.1}	{7.7}	{0.00}	{4.5}	{3.6}	{0.0}	{0.0}	{8.3}
**20	1.4	0.5	20	2.4	2.5	20	2.3	2.7	20	20	0.7

*Expected concentration ($\mu\text{g/L}$).

†Expected background concentration ($\mu\text{g/L}$).

**Approximate ratio of the spike to background concentration.

Table C4. Metal concentrations ($\mu\text{g/L}$) measured in the microwave- HNO_3 -HF digest of the RMA standard soil and NIST SRM-2704 sediment (Table 6).

<i>NIST Sediment</i>							
<i>weight (g)</i>	<i>Ba</i>	<i>Cd</i>	<i>Cu</i>	<i>Cr</i>	<i>Ni</i>	<i>Pb</i>	<i>Zn</i>
0.883	25.0	7.50	19.6	21.9	20.0	21.1	8.23
	*(10,500)	(400)	(4200)	(4200)	(2100)	(6300)	(44,100)
	†[300]	[3.42]	[94.0]	[105]	[47.9]	[152]	[414]
0.831	24.0	7.18	17.7	19.3	19.0	20.5	7.88
	(10,500)	(400)	(4200)	(4200)	(2100)	(6300)	(44,100)
	[306]	[3.49]	[90.2]	[98.4]	[48.4]	[157]	[422]
0.914	28.1	7.70	12.3	22.8	22.4	21.5	17.6
	(10,500)	(400)	(7350)	(4200)	(2100)	(6300)	(23,100)
	[310]	[3.40]	[99.7]	[106]	[51.9]	[149]	[448]

<i>RMA Soil</i>						
<i>weight (g)</i>	<i>Ba</i>	<i>Cu</i>	<i>Cr</i>	<i>Ni</i>	<i>Pb</i>	<i>Zn</i>
0.864	25.5	16.1	27.8	13.3	26.2	17.1
	(7350)	(600)	(600)	(1100)	(700)	(2100)
	[224]	[11.5]	[19.9]	[17.5]	[21.9]	[42.9]
0.719	33.3	13.6	19.0	22.4	30.9	12.4
	(12,600)	(600)	(850)	(600)	(500)	(2100)
	[602]	[11.7]	[23.2]	[19.3]	[22.2]	[37.4]
0.751	38.6	14.1	19.8	12.7	33.6	14.9
	(12,600)	(600)	(850)	(1100)	(500)	(2100)
	[668]	[11.6]	[23.1]	[19.2]	[23.1]	[43.0]

*Dilution factor (mL).

†Sediment and soil concentrations ($\mu\text{g/g}$).

Table C5. Metal concentrations ($\mu\text{g/L}$) measured in the microwave- HNO_3 -HCl digest of the NIST SRM-2704 reference sediment.

<i>Sediment weight (g)</i>	<i>Sb</i>
0.472	11.6 *(100) †[2.48]
0.498	16.4 (100) [3.32]
0.496	14.5 (100) [2.95]

*Dilution factor (mL).

†Sediment concentration ($\mu\text{g/g}$).

The digestion in Table C5 was performed with the same protocol as the other microwave digestions. Under these conditions, the 10 mL of 50/50 HNO_3 and HCl in the presence of approximately 0.5 g NIST SRM-2704 sediment exceeded the pressure limits of the digestion vessel, releasing a chlorine-nitric gas mixture. Further development of a digestion protocol for the extraction of Sb is necessary before routine application in the field. The average recovery of $2.92 \mu\text{g/g}$ is 77% of the accepted value ($3.79 \mu\text{g/g}$) reported for this reference material.

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